

Ion Dynamics near Charged Electrodes with Excluded Volume Effect

James Baker-Jarvis, Bill Riddle

Radio-Frequency Technology Division, National Institute of Standards and Technology, Boulder, CO

Albert M. Young¹

MIT Lincoln Laboratory

ABSTRACT

The goal of this paper is to analyze ion relaxation around a charged electrode taking into account finite ion volume and frequency. Time-dependent and electrostatic equations for ion behavior near an electrode are developed and include the effects of nonequilibrium and steric hindrance. Time-dependent wave equations for the potentials are developed in the Lorentz gauge. The charge density is expressed as a sum of the quasi-steady state solution plus a nonequilibrium term. For slowly changing potentials the ions are in quasi-equilibrium and we show that in this limit the potential satisfies the sinh-Gordon equation. New solutions to this nonlinear time-dependent equation are developed. In the low voltage limit the equation reduces to the Klein-Gordon equation, time-dependent analog of the Debye-Hückel equation. We also present equations for capacitance and surface charge.

1 INTRODUCTION

THE goal of this paper is to model the ion distribution in a solution around a charged electrode, including effects of both frequency and excluded volume of the ions, in order to enhance understanding of the interface. To this end we study the time-dependent concentration and potential equations [1]. We then consider the electrostatic limit and develop solutions to a modified Poisson-Boltzmann equation that includes the excluded volume.

The paper starts with a derivation of equations for the potentials with charge and current densities that depend on the potentials, then progresses into a development of a wave equation valid for a steady-state charge density, and concludes with a study of the electrostatic limit. In Section 2 we develop differential equations for time-dependent scalar and vector potentials in the Lorentz gauge. In Section 3 the charge-concentration is developed using a generalized drift-diffusion equation and is shown to separate into quasi-steady state and nonequilibrium components. The current density is expressed in terms of the ion-concentration current. Since the ions adjust position in response to an applied field, the calculation of the potential evolution is very complicated.

We obtain a system of coupled nonlinear integral-differential equations for the potentials. The time-dependent equation of motion in the quasi-static limit is shown to be the sinh-Gordon equation and solutions are developed in Sections 4 and 5. The solution we develop to the modified Poisson-Boltzmann equation in Section 6 allows a unified and ac-

curate approach to modeling both the Stern and diffuse layers (see Figure 1) with a single equation [2, 3]. Corrections are commonly made to the Poisson-Boltzmann equation by including an extra layer near the electrode, commonly called the Stern layer, that varies linearly with potential. In our theory the Stern layer is more adequately modeled since the finite volume of the ions is taken into account. This Equation reduces to the traditional Poisson-Boltzmann solution in the limit of infinitely small ions.

In Section 7 we construct equations for the surface charge density and capacitance.

2 DIFFERENTIAL EQUATIONS FOR THE POTENTIALS

In this Section we develop time-dependent differential equations for the vector and scalar potentials using time-dependent charge and current densities.

We consider a symmetric ensemble of positively and negatively charged ions near a positively charged electrode. We can develop differential equations for the scalar and vector potentials if we substitute

$$\vec{E} = -\nabla\psi - \frac{\partial\vec{A}}{\partial t} \quad (1)$$

where \vec{A} is the vector potential, into

$$\nabla \cdot \vec{D} = \rho \quad (2)$$

Table 1. List of symbols

Symbol	Meaning	Unit
\vec{A}	vector potential	V.s/m
a^3	volume of an ion	m ³
c^\pm	ion concentration	ions/m ³
c_a^\pm	quasi-steady state ion concentration	ions/m ³
c_d	capacitance per area	F/m ²
c_0	ion concentration in absence of a field	ions/m ³
\vec{D}	displacement vector	C/m ²
D_0	diffusion constant	m ² /s
$F(z)$	concentration at t=0	ions/m ³
f_0	$a^3 c_0$	
k	$k=2\pi/\lambda_D$	m ⁻¹
k_B	Boltzmann's constant	J/K
G	Green's function	
g	sources in diffusion equation	ions/m ³ .s
\vec{J}	current density	A/m ²
q	magnitude of charge on an electron	C
T	temperature	K
t	time	s
y	normalized potential	
y_e	integral of normalized electric field	
z	axial coordinate	m
z_c	valance of the ions	
ϵ	permittivity	F/m
Γ	ion flux	ions/m ² .s
Γ_0	Γ_a on boundary	ions/m ² .s
Γ_s	quasi-steady state ion flux	ions/m ² .s
λ_D	Debye-screening length	m
μ_c	mobility	m ² /V.s
ω	radial frequency	1/s
ψ	potential	V
ψ_0	potential on the electrode	V
ρ	charge density	C/m ³
σ	surface charge density	C/m ²
σ_c	solution conductivity	S/m
τ_e	relaxation time	s
μ	permeability	H/m
λ_n	eigenvalue	

and use the Lorentz gauge condition

$$\nabla \cdot \vec{A} + \epsilon \mu \frac{\partial \psi}{\partial t} = 0 \quad (3)$$

to obtain the pair of equations

$$\epsilon \mu \frac{\partial^2 \psi}{\partial t^2} - \nabla^2 \psi = \frac{\rho}{\epsilon} \quad (4)$$

$$\epsilon \mu \frac{\partial^2 \vec{A}}{\partial t^2} - \nabla^2 \vec{A} = \mu \vec{J} \quad (5)$$

where ρ is the free-charge density of the ions, \vec{J} is the current density, and ϵ and μ are the spatially independent static permittivity and magnetic permeability. It is possible to generalize the above derivation of the potential differential equation to include frequency dependence in the permittivity and permeability by using the Fourier transform of the pulse-response function as shown in Section 9.4. These generalized equations will be used in Section 5.

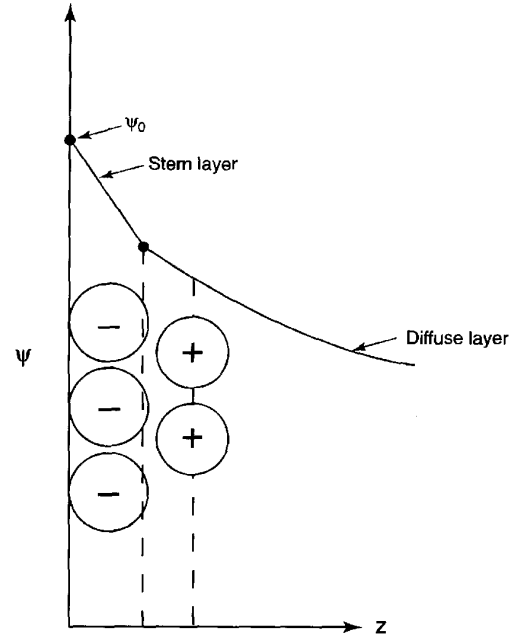


Figure 1. A positively charged, open-circuited electrode with electrolyte showing Stern and diffuse layers. ψ_0 is the potential on the electrode and z is the axial coordinate.

3 THE CHARGE CONCENTRATION

3.1 EQUATION FOR THE CONCENTRATION

The net charge density ρ , for a single species of ion, is the sum over negatively and positively charged ions [4]. The charge concentration for a symmetrical charge species can be expressed in terms of the concentration $c^\pm(\vec{r}, t)$ in units of ions per cubic meter of solute. However, the charge concentration depends on the potential.

The ions with charge $\pm q$ have a concentration c^\pm that satisfies a generalized drift-diffusion equation in potentials $\psi(\vec{r}, t)$ and $\vec{A}(\vec{r}, t)$. The charge density for a symmetrical species is

$$\rho(\vec{r}, t) = z_c q [c^+(\vec{r}, t) - c^-(\vec{r}, t)] \quad (6)$$

where z_c is the valency per ion, and q the magnitude of the electron charge. The \pm signs indicate the charge of the ion. The concentration in the absence of a field is c_0 . As we will see in Section 3, the charge density has both quasi-steady state and nonequilibrium components.

The current density is expressed in terms of the ion-flux densities $\vec{\Gamma}^\pm$ that contains both diffusion and drift currents

$$\vec{J}(\vec{r}, t) = z_c q [\vec{\Gamma}^+(\vec{r}, t) - \vec{\Gamma}^-(\vec{r}, t)] \quad (7)$$

The potentials can be calculated once the charge and current densities are known, but the problem is that the charge and current densities depend on the potentials.

The ion concentration $c^\pm(\vec{r}, t)$ satisfies the drift-diffusion equation

$$\frac{\partial c^\pm(\vec{r}, t)}{\partial t} + \nabla \cdot \vec{\Gamma}^\pm = g^\pm \quad (8)$$

Equation (8) describes charge conservation with possible sources g^\pm for creation or recombination of charge. Once c^\pm is found it can be used to form the charge density (6) and current density (7). In equilibrium the concentration is simply given by the Boltzmann distribution.

The current density will be developed below. The initial and boundary conditions on (8) are

1. Initial condition $c^\pm(\vec{r}, 0) = F^\pm(\vec{r})$, usually $c^\pm(\vec{r}, 0) = c_0$.
2. $\vec{\Gamma}^\pm$ on electrode is specified.
3. $c^\pm(0, t)$ or $c^\pm(r \rightarrow \infty, t)$ specified from the behavior of $\psi(\vec{r}, t)$ and $\vec{A}(\vec{r}, t)$ as $r \rightarrow \infty$.

The volume of the ions can influence the potential near the electrode where the concentration is high. Wiegel [5] derived an expression for the drift-diffusion current given an effective charge concentration which has finite volume.

In order to take into account the volume of the ions we use Wiegel's result for the drift-diffusion current [5] (see Section 9.2 for derivation)

$$\vec{\Gamma}^\pm(z, t) = D_0 \left[\underbrace{-\nabla c^\pm}_{\text{diffusion}} - \underbrace{\frac{c^\pm a^3 \nabla(c^+ + c^-)}{1 - a^3(c^+ + c^-)}}_{\text{steric hindrance}} \right. \\ \left. \pm \underbrace{\frac{z_c q \vec{E} c^\pm}{k_B T}}_{\text{electric interaction}} \pm \underbrace{\frac{z_c q \vec{v} \times (\nabla \times \vec{A}) c^\pm}{k_B T}}_{\text{magnetic interaction}} \right] \quad (9)$$

where a^3 is an ion volume and D_0 the diffusion constant. We assume equal diffusion constants $D_0^+ = D_0^- = D_0$. The electric field \vec{E} is related to the scalar and vector potentials by (1). The steric-hindrance term is nonlinear in concentration. In our analysis we neglect the magnetic-force interaction.

In one-dimensional rectangular coordinates, assuming only an E_z electric field we have only an A_z vector potential component and a z -component of the ion flux

$$\Gamma_z^\pm = D_0 \left[-\frac{\partial c^\pm}{\partial z} - \frac{c^\pm a^3}{1 - a^3(c^+ + c^-)} \frac{\partial(c^+ + c^-)}{\partial z} \pm \frac{z_c q}{k_B T} E_z c^\pm \right] \quad (10)$$

In the limit of volume-less ions ($a^3 = 0$), (8) and (10) reduce in one spatial coordinate to

$$\frac{\partial c^\pm(z, t)}{\partial t} + D_0 \frac{\partial}{\partial z} \left[-\frac{\partial c^\pm(z, t)}{\partial z} \pm \frac{z_c q E_z}{k_B T} c^\pm(z, t) \right] = 0 \quad (11)$$

In developing a solution to (8) we consider the quasi-steady state concentration $c_s^\pm(z, t)$ which is a solution of the auxiliary problem $\nabla \cdot \vec{\Gamma}_s^\pm = g^\pm$. We use the term 'quasi-steady state' since time is contained in this equation only as a parameter. We will show that the solution to (8) can be developed in terms of the quasi-steady state solution (58) as shown in the Appendix Section 9.2. The boundary conditions for the quasi-steady state solution, with the possible exception of the initial condition, are generally the same as given above for (8).

The first three terms in (59) of the Appendix, Section 9.2, are

$$c^\pm(z, t) = c_s^\pm(z, t) + \int dz' (z, t, z', 0) [F^\pm(z') - c_s^\pm(z', 0)] \\ - 2 \int_0^t d\tau \int dz' \frac{dc_s^\pm(y_e(z', \tau))}{dy_e} \frac{\partial y_e}{\partial \tau} G(z, t, z', \tau) + \dots \quad (12)$$

where G is Green's function in which the solution is expanded. Generally, $F^\pm = c_s^\pm(t = 0) = c_0$, and thus the first integral term on the right hand side of (12) vanishes. The advantage of (12) is that only the quasi-steady state solution is required and allows a study of the frequency dependence. The boundary condition on the electrodes is satisfied by the quasi-steady state term which is the first term on the right hand side of (12) since the derivative of Green's function vanishes on the electrodes.

The normalized potential is

$$y_e(z, t) = -\frac{z_c q}{k_B T} \int_0^z E_z(z', t) dz' + y_0(t) \quad (13)$$

where the normalized potential on the boundary is

$$y_0(t) = \frac{z_c q}{k_B T} \left[\psi(0, t) + \frac{\partial}{\partial t} \int A_z dz (0, t) \right] \quad (14)$$

and

$$\frac{\partial y_e}{\partial t} = -\frac{z_c q}{k_B T} \frac{\partial}{\partial t} \int_0^z E_z dz' + \frac{\partial y_0}{\partial t} \\ = \frac{z_c q}{k_B T} \int_0^z \frac{J_z(z', t)}{\epsilon} dz' + \frac{\partial y_0}{\partial t} \quad (15)$$

If we neglect the vector potential this reduces to

$$y_e(z, t) = \frac{z_c q \psi(z, t)}{k_B T} \quad (16)$$

The Fourier transform of (12) is worked out in the Appendix, Section 9.3.

There are two cases of primary interest. In the special cases where $\Gamma_0^\pm = 0$, that is for an open-circuited electrode, and for specified ion-flux density Γ_0^\pm , we present analytical solutions for c_s^\pm . In both of these special cases we assume there are no source terms.

3.1.1 QUASI-STEADY STATE SOLUTION FOR AN OPEN-CIRCUITED ELECTRODE

The quasi-steady state solution is required as input to (12). For open-circuited conditions we assume an electrode positioned at $z = 0$, extending to ∞ , and variations only in the z coordinate (see Figure 1); then (58) is solved subject to boundary conditions.

The quasi-steady state solution for open-circuited conditions ($\Gamma_0^\pm = 0$) that satisfies the two following boundary conditions

$$\lim_{z \rightarrow \infty} c_s^\pm(z) = c_0$$

$$-\frac{\partial c_s^\pm(0, t)}{\partial z} - \frac{a^3 c_s^\pm(0, t)}{1 - a^3(c_s^+(0, t) + c_s^-(0, t))} \times$$

$$\frac{\partial(c_s^+(0, t) + c_s^-(0, t))}{\partial z} \pm \frac{E_z}{k_B T} c_s^\pm(0, t) = 0$$

is

$$c_s^\pm(z, t) = \frac{c_0 \exp(\mp y_e)}{1 + 4f_0 \sinh^2(y_e/2)} \quad (18)$$

where $f_0 = c_0 a^3$. In the limit of neglecting ion volume we have a Boltzmann distribution

$$c_s^\pm(z, t) = c_0 \exp(\mp y_e) \quad (19)$$

Green's function G for this case is worked out in the Appendix, Section 9.2. The charge density (6) is given through use of (12), assuming $c^\pm(t=0) = c_s^\pm(t=0) = c_0$.

$$\rho(z, t) = -2z_c q \frac{c_0 \sinh(y_e)}{1 + 4f_0 \sinh^2(y_e/2)}$$

$$- 2z_c q \int_0^t d\tau \int_0^\infty dz' \left[\frac{dc_s^+(z', \tau)}{dy_e} - \frac{dc_s^-(z', \tau)}{dy_e} \right] \times$$

$$\frac{\partial y_e}{\partial \tau} G(z, t, z', \tau) + \dots \quad (20)$$

This charge density is a nonlinear function of potential.

3.1.2 QUASI-STEADY STATE SOLUTION FOR SPECIFIED CURRENT FROM THE ELECTRODE

We consider now the problem for the quasi-steady state solution for a ion-flux density flowing between two electrodes at $z = 0$ and $z = L$ which are at different potentials (see Figure 2). In order to obtain an analytical solution we first neglect the effects of ion volume.

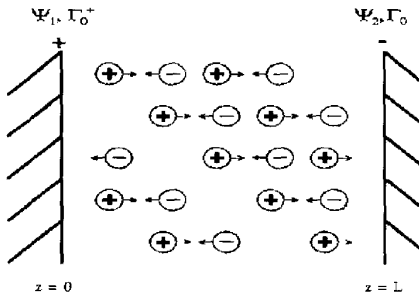


Figure 2. Two electrodes at different potentials ψ_1 and ψ_2 separated by an electrolyte solution with current Γ_0^\pm flowing.

We assume the following initial and boundary conditions are to be satisfied in $z \in [0, L]$. For the initial conditions $c_s^\pm = c_0$, $\psi = 0$ and $\Gamma_0^\pm = 0$, and

$$-\frac{\partial c_s^\pm(0, t)}{\partial z} \pm \frac{z_c q E_z}{k_B T} c_s^\pm(0, t) = \frac{\Gamma_0^\pm}{D_0} \quad (21)$$

the quasi-steady state solution to the ion-flux density in (58) neglecting ion volume is

$$c_s^\pm(z, t) = c_0 \exp(\mp y_e(z, t))$$

$$- \frac{\Gamma_0^\pm(t)}{D_0} \exp(\mp y_e(z, t)) \int_0^z \exp(\pm y_e(z', t)) dz' \quad (22)$$

We can also obtain a solution that includes ion volume by making a single assumption: $\Gamma_0^\pm(t)/(1 - a^3(c_s^+ + c_s^-)) \approx \Gamma_0^\pm(t)$. This assumption is reasonable. The solution with ion volume, denoted by c_{si}^\pm , is

$$c_{si}^\pm(z, t) = \frac{c_s^\pm(z, t)}{1 + a^3(c_s^+(z, t) + c_s^-(z, t))} \quad (23)$$

where c_s^\pm are solutions of (22).

Green's function to be used in (12) in this case is

$$G(z, t, z', \tau) = \frac{2}{L} \sum_{n=0}^{\infty} U(t - \tau) \exp[-D_0 \lambda_n^2 (t - \tau)] \times$$

$$\cos\left(\frac{n\pi z}{L}\right) \cos\left(\frac{n\pi z'}{L}\right) \quad (24)$$

where U is the unit-step function.

3.2 RELATIVE IMPORTANCE OF QUASI-STATIC AND NONEQUILIBRIUM TERMS

Memory is important in the charge density because of the finite diffusion rate and conductivity. If the potential changes slowly and/or the diffusion constant or conductivity is large, then from (12) we can see that the steady state dominates. In this approximation, concentration for time-dependent potentials is just the first term in (12) and the charge-concentration density is given by (6). Equation (63) indicates that the nonequilibrium term becomes less important as $D_0/\omega \gg \lambda_D^2$ where we identify the relevant length λ_D as the Debye screening length. The reciprocal of the Debye screening length is $k = 1/\lambda_D$ and is given by

$$k^2 = \frac{2c_0 z_c^2 q^2}{\epsilon k_B T} \quad (25)$$

If we use the Drude model for the conductivity $\sigma_c = 2q c_0 \mu_c$, where μ_c is the mobility which is related to the diffusion constant through $\mu_c = q D_0 / k_B T$ we get an expression for the characteristic relaxation time or frequency as

$$\omega = \frac{1}{\tau_e} \ll \frac{D_0}{2\lambda_D^2} = \frac{\sigma_c}{\epsilon} \quad (26)$$

Dukhin and Shilov ([7], Equation III-88) and Grosse [1] give a similar constraint in a quasi-equilibrium approximation. Basically (26) is indicating that highly conductive and diffusive fluids have a faster relaxation time. For example, if the fluid has $\sigma_c = 100 \mu S$ and $\epsilon = 100 \epsilon_0$ then $\omega \ll 1 \times 10^5$ rad/s.

4 POTENTIAL EQUATIONS AT LOW FREQUENCIES

In this Section we develop the potential in the quasi-static limit. When (20) is substituted into (4) an integral-differential equation for the potential in terms of the quasi-steady state solution is obtained which

includes nonequilibrium effects and excluded volume

$$\begin{aligned} \varepsilon\mu \frac{\partial^2 y}{\partial t^2} - \frac{\partial^2 y}{\partial z^2} &= \frac{z_c^2 q^2}{\varepsilon k_B T} [c_s^+(y_e) - c_s^-(y_e)] \\ &- \frac{2z_c^2 q^2}{\varepsilon k_B T} \int_0^t d\tau \int dz' \left[\frac{dc_s^+(z', \tau)}{dy_e} - \frac{dc_s^-(z', \tau)}{dy_e} \right] \times \\ &\quad \frac{\partial y_e}{\partial \tau} G(z, t, z', \tau) + \dots \end{aligned} \quad (27)$$

where we have retained only derivatives of the axial coordinate, and

$$y = \frac{z_c q \psi(z, t)}{k_B T} \quad (28)$$

We specify for (27) an initial condition and potential or electric field both on the electrodes and as $z \rightarrow \infty$. In addition we have an equation for the z -component of the vector potential

$$\varepsilon\mu \frac{\partial^2 A_z}{\partial t^2} - \frac{\partial^2 A_z}{\partial z^2} = \mu z_c q [\Gamma_z^+(z, t) - \Gamma_z^-(z, t)] \quad (29)$$

where the current density is given by (7) and (9). To summarize we have developed equations describing the scalar and vector potentials in an ion solution as a function of frequency. The solution proceeds by solving (58) for the quasi-steady state solution and then (8), (27), and (29) simultaneously for c^\pm , ψ and A_z . In principle the magnetic field could be included in which case all vector potential components must be determined. In the approximation of low frequencies and high diffusion constant the quasi-steady state concentration is a reasonable approximation for the limits in (26). In this limit we obtain the following expression for the charge density for an open-circuited electrode, neglecting ion volume

$$\rho(z, t) = -2z_c q c_0 \sinh y(z, t) \quad (30)$$

and therefore the inhomogeneous wave equation is

$$-\varepsilon\mu \frac{\partial^2 y}{\partial t^2} + \frac{\partial^2 y}{\partial z^2} = k^2 \sinh y \quad (31)$$

Note that the low-frequency approximation excludes nonequilibrium effects and thereby simplifies the analysis. In a more general treatment (27) should be solved numerically.

Equation (31) is the sinh-Gordon equation which is equivalent to the sine-Gordon equation of an imaginary argument. Unlike the sine-Gordon equation, the sinh-Gordon one does not have soliton solutions. A linear approximation of (31) allows a time-harmonic solution.

5 SOLUTION OF THE TIME-DEPENDENT, QUASI-STATIC POTENTIAL EQUATION

It is possible to develop an analytic solution to (31). The solution to (31) for open-circuit conditions is

$$\begin{aligned} y(z, t) &= \Re \left[4 \operatorname{arctanh} \left[\tanh(y_0/4) \right] \right. \\ &\quad \times \exp \left(-z \sqrt{k^2 - \omega^2 \varepsilon \mu} \right) \exp(i\omega t) \left. \right] \end{aligned} \quad (32)$$

where

$$y_0 = \frac{z_c q \psi_0}{k_B T} \quad (33)$$

This solution is time harmonic at low voltage. The real part of the function is denoted by \Re , also ε and μ here are static values. Equation (32)

can also be expressed as

$$y(z, t) = \Re \ln \left[\frac{e^{\frac{y_0}{2}} + 1 + (e^{\frac{y_0}{2}} - 1)e^{-z \sqrt{k^2 - \omega^2 \varepsilon \mu}} e^{i\omega t}}{e^{\frac{y_0}{2}} + 1 - (e^{\frac{y_0}{2}} - 1)e^{-z \sqrt{k^2 - \omega^2 \varepsilon \mu}} e^{i\omega t}} \right] \quad (34)$$

At $z = 0$ we have

$$y(0, t) = \Re \ln \left[\frac{e^{\frac{y_0}{2}} + 1 + (e^{\frac{y_0}{2}} - 1)e^{i\omega t}}{e^{\frac{y_0}{2}} + 1 - (e^{\frac{y_0}{2}} - 1)e^{i\omega t}} \right] \quad (35)$$

In the low-voltage limit ($y \ll 1$), $\sinh y$ reduces to y and we obtain the Klein-Gordon equation, the time-dependent analog of the Debye-Hückel equation

$$-\varepsilon\mu \frac{\partial^2 y}{\partial t^2} + \frac{\partial^2 y}{\partial z^2} = k^2 y \quad (36)$$

The frequency-domain solution in one spatial dimension to the Klein-Gordon equation which includes dispersive material properties (see Appendix, Section 9.4)

$$y(z, \omega) = y_0 \exp \left(-z \sqrt{k^2 - \omega^2 \varepsilon^*(\omega) \mu^*(\omega)} \right) \quad (37)$$

Equation (37) has a cutoff frequency when $k^2 < \omega^2 \varepsilon \mu$ or $f_c = k/(2\pi\sqrt{\varepsilon\mu})$, where k^2 is given by (25). For $f < f_c$ the solution is exponentially damped; otherwise, it is sinusoidal. The cutoff frequency is very high and the low-frequency assumption breaks down before it is reached. In the limit of small potential, the frequency component of (32) reduces to (37).

If we incorporate the excluded volume in the source term in (4) we have

$$-\varepsilon\mu \frac{\partial^2 y}{\partial t^2} + \frac{\partial^2 y}{\partial z^2} = \frac{k^2 \sinh y}{1 + 4f_0 \sinh^2(y/2)} \quad (38)$$

Due to the symmetry in z and t we can use the change of variable $\alpha = -i\omega t + z \sqrt{k^2 - \omega^2 \varepsilon \mu}$ to write

$$\frac{dy}{d\alpha} = -\frac{1}{\sqrt{f_0}} \sqrt{\ln(1 + 4f_0 \sinh^2(y(\alpha)/2))} \quad (39)$$

We can approximately integrate (39) in the limit of $y \ll 1$ to obtain

$$y(z, t) \approx y_0 e^{-\alpha} \left[1 + \frac{1}{2}(1 - e^{-2\alpha}) y_0^2 (1 - 6f_0) \right] \quad (40)$$

6 MODIFIED POISSON-BOLTZMANN EQUATION WITH EXCLUDED VOLUME

In this Section we consider the electrostatic limit of (27) in rectangular coordinates. A review of the solution to the Poisson-Boltzmann equation is given in Section 9.5. Here we derive an analytical solution for the potential distribution. The inclusion of the volume of the ions allows the region near the electrode to saturate, thereby changing the potential distribution. The finite volume of the ions produces charge separation at the electrode and decreases the potential decay.

In rectangular coordinates using the charge density (6) we find

$$\frac{d^2 y}{dz^2} = \frac{k^2 \sinh y}{1 + 4f_0 \sinh^2(y/2)} \quad (41)$$

and in the limit as $a^3 \rightarrow 0$ we obtain (72).

We can integrate (41) to obtain

$$\left(\frac{dy}{dz}\right)^2 = 2 \int_0^y k^2 \frac{\sinh z}{1 + 4f_0 \sinh^2(z/2)} dz \quad (42)$$

$$= 2z_0^2 \ln(1 + 4f_0 \sinh^2(y/2))$$

where $z_0 = \sqrt{z_c^2 q^2 / k_B T a^3 \epsilon}$, or

$$\frac{dy}{dz} = \mp z_0 \sqrt{2 \ln(1 + 4f_0 \sinh^2(y/2))} \quad (43)$$

The \mp signs are for $\pm y_0$ respectively. This solution (43) stands in contrast to the solution of the Poisson-Boltzmann equation (76).

In order to verify that (43) reduces to the Poisson-Boltzmann solution (76) in the limit of small f_0 , consider a Taylor series expansion of (43) for small a^3

$$\frac{dy}{dz} = -z_0 \left[2f_0^{1/2} \sqrt{2} \sinh \frac{y}{2} - 2a^3 f_0^{3/2} \sqrt{2} \sinh^3 \frac{y}{2} + \frac{13}{3} a^6 f_0^{5/2} \sqrt{2} \sinh^5 \frac{y}{2} + O(a^9) \right] \quad (44)$$

To first order this reduces to the Poisson-Boltzmann solution (76), since $k = \sqrt{2} z_0 \sqrt{f_0}$. Consider the limit as $y \rightarrow \infty$; we see the modified equation for dy/dz (43) scales in proportion to y , whereas the Poisson-Boltzmann equation scales as $k \sinh(y/2)$. In the low-field limit both expressions scale in proportion to y . The difference is the result of charge saturation at the interface. As charge builds up at the interface the finite volume produces charge separation.

In general, the integral of (43) cannot be evaluated analytically. However, in the case of two terms in the Taylor series expansion of (43), we can integrate to obtain

$$-kz = \int_{y_0}^y \frac{d\theta}{2 \sinh(\theta/2) - 2f_0 \sinh^3(\theta/2)} \quad (45)$$

$$= \ln \frac{\tanh(y/4)}{\tanh(y_0/4)} + \frac{\sqrt{f_0} \tanh^{-1} \frac{\sqrt{f_0} \cosh(y/2)}{\sqrt{1+f_0}}}{\sqrt{1+f_0}}$$

$$- \frac{\sqrt{f_0} \tanh^{-1} \frac{\sqrt{f_0} \cosh(y_0/2)}{\sqrt{1+f_0}}}{\sqrt{1+f_0}}$$

This Equation reduces to the Poisson-Boltzmann solution (77) when $f_0 \rightarrow 0$.

7 SURFACE CHARGE AND CAPACITANCE

The surface charge density σ depends on both the scalar and vector potentials. In one space dimension the electrostatic surface charge density at the electrode is

$$\sigma = -\epsilon \frac{\partial \psi_0}{\partial z} \quad (46)$$

The differential capacitance per unit area is

$$C_d = \frac{\partial \sigma(\psi_0)}{\partial \psi_0} \quad (47)$$

The surface charge with excluded volume is

$$\sigma = - \int_0^\infty \rho(x) dx = -\epsilon \frac{d\psi_0}{dz}(z=0) \quad (48)$$

$$= \frac{\epsilon k_B T}{z_c q} \sqrt{2z_0^2 \ln \left(1 + 4f_0 \sinh^2 \left(\frac{z_c q \psi_0}{2k_B T} \right) \right)}$$

The differential capacitance with excluded volume is

$$C_d = \frac{d\sigma}{d\psi_0}$$

$$= \frac{2\epsilon z_0 f_0 \sqrt{2} \sinh \left(\frac{z_c q \psi_0}{2k_B T} \right) \cosh \left(\frac{z_c q \psi_0}{2k_B T} \right)}{\left(1 + 4f_0 \sinh^2 \left(\frac{z_c q \psi_0}{2k_B T} \right) \right) \sqrt{\ln \left(1 + 4f_0 \sinh^2 \left(\frac{z_c q \psi_0}{2k_B T} \right) \right)}} \quad (49)$$

These results can be compared to the Poisson-Boltzmann surface charge density and capacitance equations

$$\sigma = 2\sqrt{2k_B T \epsilon c_0} \sinh \left(\frac{z_c q \psi_0}{2k_B T} \right) \quad (50)$$

and

$$C_d = \sqrt{2 \frac{z_c^2 q^2 \epsilon c_0}{k_B T}} \cosh \left(\frac{z_c q \psi_0}{2k_B T} \right) \quad (51)$$

In the limit as $\psi_0 \ll 1$ (49) and (51) yield equivalent results. Equations (50) and (51) do not yield physical results since they both increase exponentially with ψ_0 .

8 NUMERICAL RESULTS AND CONCLUSIONS

We have developed time-dependent wave equations for the potentials and equations for the charge density. We have shown that in the limit of slowly varying potentials or for solvents with large diffusion constants, the quasi-static charge distribution is a good approximation when $\omega \ll \sigma_c / \epsilon$. We then developed solutions to the sinh-Gordon equation for this quasi-static charge distribution.

In order to study the effects of the excluded volume, in Figures 3 to 5 we plot the potentials in the static limit for both the Poisson-Boltzmann and modified equations, assuming $f_0 = 0.05$. In each case the potential is specified at the boundary on $z = 0$. The modified Poisson-Boltzmann results were obtained by numerically integrating (43).

At HV there is a significant difference between results. This difference decreases as ψ_0 decreases. In order to study the concentration dependence on the potential in Figure 6 we plot the potentials as a function of distance from the interface for different excluded volumes.

In Figures 7 and 8 we contrast the solutions for the surface charge and capacitance.

Including the volume of the ions allows the modeling of the Stern and diffuse layers in a unified way. The finite volume of ions allows the Stern layer to saturate whereas the solutions of the Poisson-Boltzmann equation yield expressions for the surface charge density and capacitance that diverge exponentially as the potential increases. Measurements indicate that the capacitance does not rise exponentially as potential increases [8]. We see in Figure 8 that for a finite volume of ions the slope

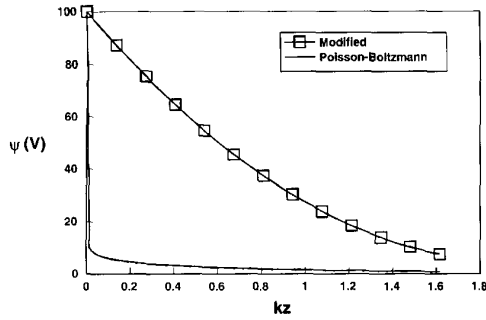


Figure 3. Potential as a function of normalized distance for the Poisson-Boltzmann and modified equations, $\psi_0 = 100$ V. The modified Poisson-Boltzmann equation plotted is the numerical integration of (43) which includes the effects of ion volume ($f_0 = 0.05$). The solution to the Poisson-Boltzmann equation is given by (78).

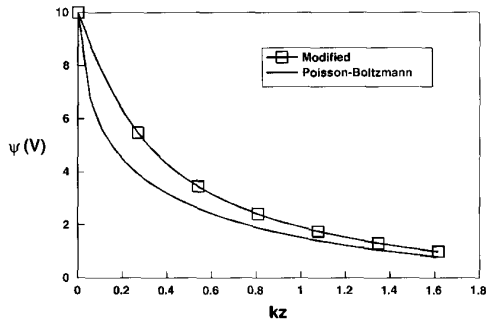


Figure 4. Potential as a function of normalized distance for the Poisson-Boltzmann and modified equations, $\psi_0 = 10$ V. The modified Poisson-Boltzmann equation plotted is the numerical integration of (43) which includes the effects of ion volume ($f_0 = 0.05$). The solution to the Poisson-Boltzmann equation is given by (78).

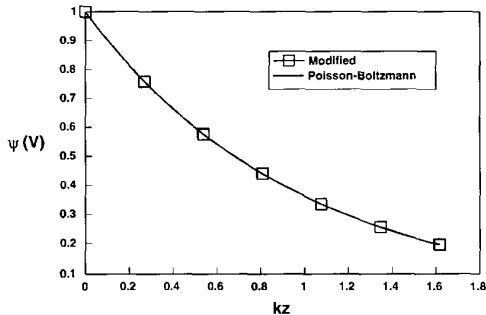


Figure 5. Potential as a function of normalized distance for the Poisson-Boltzmann and modified equations, $\psi_0 = 1$ V. The modified Poisson-Boltzmann equation plotted is the numerical integration of (43) which includes the effects of ion volume ($f_0 = 0.05$). The solution to the Poisson-Boltzmann equation is given by (78).

of the capacitance curve decreases as voltage increases. As the ion volume decreases, the solution approaches that of the Poisson-Boltzmann equation.

The time-dependent normalized potential is plotted as a function of distance from the electrode *vs.* time in Figure 9. The following conditions were used in the numerical calculations:

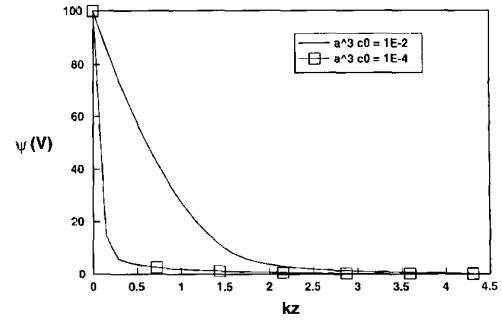


Figure 6. Effect of ion volume on potential as a function of normalized distance for the modified Poisson-Boltzmann

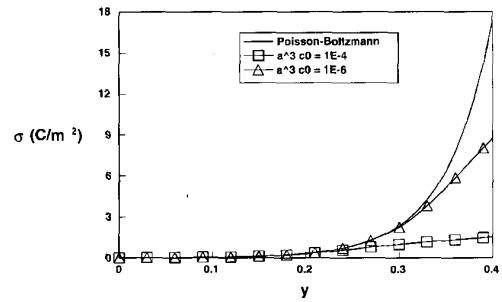


Figure 7. Comparison of the surface charge density in C/m^2 from the Poisson-Boltzmann and modified Poisson-Boltzmann equations *vs.* normalized potential.

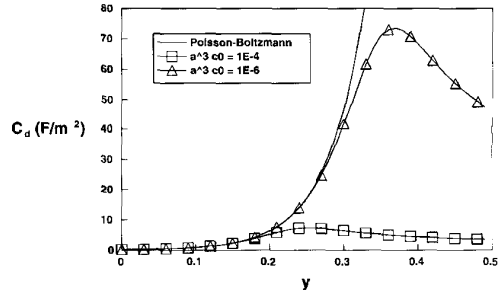


Figure 8. Comparison of the capacitance per unit area from the Poisson-Boltzmann and modified Poisson-Boltzmann equations *vs.* normalized potential.

1. The initial condition was the static Poisson-Boltzmann potential.
2. The solution and its derivative vanishes at ∞ .

The time-dependent equation allows the modeling of frequency-dependent behavior near an electrode. We used the following parameters in the plot in Figure 9: $\epsilon_r = 15$, $k = 5 \times 10^8$, $f = 1 \times 10^6$, $y_0 = 1$. We see in Figure 9 that the potential is time harmonic at low voltages and nonlinear at HV.

To summarize we have developed equations to describe the time-varying potentials around an electrode which includes the volume of ions. The charge density has been developed as a nonlinear function of potential and has both steady-state and nonequilibrium components. In the case of fast-relaxing fluids, at low frequencies the quasi-static term dominates. We give a constraint on frequency and diffusion constant

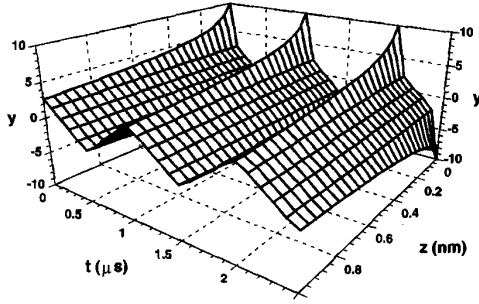


Figure 9. Time-dependent normalized potential as a function of distance and time.

where the quasi-steady state approximation is valid. A similar constraint was derived by Dukhin and Shilov [7] for a more simplified approach. We have also developed an equation at the electrostatic limit for the potential that includes the excluded volume. This solution was shown to reduce to the Poisson-Boltzmann result in the limit of neglecting ion volume.

9 APPENDICES

9.1 DIFFUSION EQUATION FOR FINITE-VOLUME IONS

If the ions in solution are assumed to have a finite volume the density determined after subtracting out the ion volume from the fluid is higher than the density determined by assuming volume-less ions. This concentration difference modifies the concentration flux by increasing the gradient. The ion volume also decreases the diffusion coefficient by decreasing the mean free path. Due to these two competing effects the diffusive flux is modified [9]. The net result is an additional steric diffusion term due to ion volume. This term has the same sign as the normal diffusion term $-\nabla c$ since the ion volume increases the effective particle gradient. We now derive the drift-diffusion current with ion volume. Let

$$\vec{\Gamma}^{\pm} = -D(c)\vec{j}_c + \frac{D_0 z_c q \vec{E}}{k_B T} c^{\pm} \quad (52)$$

assuming

$$\vec{j}_c = \nabla \left[\frac{c^{\pm}}{1 - a^3(c^{+} + c^{-})} \right] \quad (53)$$

and

$$D(c) = D_0(1 - a^3(c^{+} + c^{-})) \quad (54)$$

Using (53) and (54) we obtain

$$-D(c)\vec{j}_c = -D_0 \nabla c^{\pm} - \frac{D_0 c^{\pm} a^3}{1 - a^3(c^{+} + c^{-})} \nabla(c^{+} + c^{-}) \quad (55)$$

and therefore

$$\begin{aligned} \vec{\Gamma}^{\pm} = & -D_0 \nabla c^{\pm} - \frac{D_0 c^{\pm} a^3}{1 - a^3(c^{+} + c^{-})} \nabla(c^{+} + c^{-}) \\ & + \frac{D_0 z_c q \vec{E}}{k_B T} c^{\pm} \end{aligned} \quad (56)$$

9.2 DIFFUSION EQUATION FOR ION FLUX

9.2.1 STEADY STATE FUNCTION

The quasi-steady state solution c_s is the solution of the following one-dimensional equation

$$-D_0 \frac{\partial^2 c_s^{\pm}}{\partial z^2} = D_0 \frac{\partial}{\partial z} \left[\frac{c_s^{\pm} a^3}{1 - a^3(c_s^{+} + c_s^{-})} \frac{\partial(c_s^{+} + c_s^{-})}{\partial z} \mp \frac{z_c q}{k_B T} E_z c_s^{\pm} \right] - g^{\pm} \quad (57)$$

or by integration

$$\begin{aligned} -\frac{\partial c_s^{\pm}}{\partial z} = & \frac{c_s^{\pm} a^3}{1 - a^3(c_s^{+} + c_s^{-})} \frac{\partial(c_s^{+} + c_s^{-})}{\partial z} \\ & \mp \frac{z_c q}{k_B T} E_z c_s^{\pm} - \frac{1}{D_0} \int_0^z g^{\pm}(z', t) dz' + \frac{\Gamma_0^{\pm}}{D_0} \end{aligned} \quad (58)$$

where Γ_0^{\pm} are integration constants determined by boundary conditions on the ion-flux density.

The solution of (8) is found as an expansion in terms of the quasi-steady state solution. The advantage of this approach is that only the much simpler steady-state equation needs to be solved. Assuming the initial condition is F^{\pm} we have

$$\begin{aligned} c^{\pm}(z, t) - c_s^{\pm}(z, t) = & \int dz' G(z, t, z', 0) [F^{\pm}(z') - c_s^{\pm}(z', 0)] \\ & - 2 \int_0^t d\tau \int dz' \frac{\partial c_s^{\pm}(z', \tau)}{\partial \tau} G(z, t, z', \tau) \\ & + \int_0^t d\tau \int dz' \int_0^{\tau} d\theta \int dz'' \frac{\partial^2 c_s^{\pm}(z'', \theta)}{\partial \theta^2} G(z', \tau, z'', \theta) \times \\ & G(z, t, z', \tau) + \dots \end{aligned} \quad (59)$$

Truncation of (59) after the second term is valid at sufficiently low frequencies. Green's function satisfies

$$-\frac{\partial G(t, z, \tau, z')}{\partial \tau} = D_0 \frac{\partial^2 G(t, z, \tau, z')}{\partial z'^2} + \delta(z - z') \delta(t - \tau) \quad (60)$$

which is solved with Neumann boundary conditions on electrodes.

9.2.2 GREEN'S FUNCTION FOR OPEN-CIRCUITED ELECTRODE

The solution to (8) for $z \in [0, \infty]$ expressed in terms of the quasi-steady state solution (58) [6] for an open-circuited termination can be obtained using a cosine transform. The Green function used in (12) for

this case is

$$G(z, t, z', \tau) = \frac{2}{\pi} \int_0^\infty U(t - \tau) \cos(\lambda z) \cos(\lambda z') \times \exp(-D_0 \lambda^2 (t - \tau)) d\lambda = U(t - \tau) \times \frac{\sqrt{\pi} \left[\exp\left(-\frac{(z-z')^2}{4D_0(t-\tau)}\right) + \exp\left(-\frac{(z+z')^2}{4D_0(t-\tau)}\right) \right]}{4\sqrt{D_0(t-\tau)}} \quad (61)$$

9.3 FOURIER TRANSFORM OF THE CONCENTRATION

The Fourier transform can be taken of (12) by the convolution theorem. We need the Fourier transform to study the frequency constraints on our theory. Also helpful is the following identity

$$\frac{\sqrt{\pi}}{\sqrt{D_0 t}} \exp\left(-\frac{x^2}{4D_0 t}\right) = \int_{-\infty}^\infty \exp(-D_0 \beta^2 t - i\beta x) d\beta \quad (62)$$

The Fourier transform of c^\pm , denoted by \sim , is

$$c^\pm(z, \omega) = c_s^\pm(z, \omega) + 2i\sqrt{\frac{\omega}{16iD_0}} \int_0^\infty dz' c_s^\pm(z', \omega) \times \left[\cosh \sqrt{\frac{i(z-x')^2 \omega}{D_0}} - \sinh \sqrt{\frac{i(z-x')^2 \omega}{D_0}} + \cosh \sqrt{\frac{i(z+z')^2 \omega}{D_0}} - \sinh \sqrt{\frac{i(z+z')^2 \omega}{D_0}} \right] \quad (63)$$

Note that the relevant length is given by $\sqrt{D_0/\omega}$.

9.4 GENERALIZED WAVE EQUATION

In order to derive an equation that allows frequency dependence in permittivity and permeability it is necessary to write \vec{D} and the Lorentz gauge condition as convolutions in the form

$$\vec{D}(t) = \int_0^\infty f(\tau) \vec{E}(t - \tau) d\tau = - \int_0^\infty f(\tau) \left[\nabla \psi(t - \tau) + \frac{\partial \vec{A}(t - \tau)}{\partial t} \right] d\tau \quad (64)$$

where

$$\varepsilon^*(\omega) = \int_{-\infty}^\infty f(\tau) \exp(-i\omega\tau) d\tau \quad (65)$$

and

$$\nabla \cdot \vec{A}(t) = - \int_0^\infty g(\tau) \frac{\partial \psi}{\partial t}(t - \tau) d\tau \quad (66)$$

where

$$\varepsilon^*(\omega) \mu^*(\omega) = \int_{-\infty}^\infty g(\tau) \exp(-i\omega\tau) d\tau \quad (67)$$

Therefore

$$\nabla \cdot \vec{D}(t) = - \int_0^\infty f(\tau) \left[\nabla^2 \psi(t - \tau) + \nabla \cdot \frac{\partial \vec{A}(t - \tau)}{\partial t} \right] d\tau \quad (68)$$

Now consider the Fourier transform of (68) in the low-field limit and the use of (66). In the frequency domain ε^* , where * denotes frequency-domain complex permittivity, is a function of ω . In the frequency domain the wave equation is

$$\varepsilon^*(\omega) \mu^*(\omega) \omega^2 \tilde{y} + \nabla^2 \tilde{y} = k^2(\omega) \widetilde{\sinh y} \quad (69)$$

Note that the tilde is over the entire $\sinh y$.

9.5 POISSON-BOLTZMANN EQUATION

In this Section we review the electrostatic theory for ions in an applied potential neglecting ion volume. In this limit we let both the ion volume and frequency go to zero. The time-independent version of (31) for infinitely small ions is the Poisson-Boltzmann equation [10], which is commonly used for modeling the ion atmosphere around a charged object [10–12]. If we assume a positively charged electrode then the positive ions in the solution are counterions and the negatively charged ions are co-ions. The concentration of ions follows Boltzmann statistics

$$c^\pm = c_0 \exp\left(\mp \frac{z_c q \psi}{k_B T}\right) \quad (70)$$

These distributions indicate that there is high probability of negative ions residing near the electrode and a low probability of co-ions residing near the electrode.

The potential satisfies

$$\nabla^2 \psi + \frac{\rho}{\varepsilon} = 0 \quad (71)$$

The Poisson-Boltzmann equation (71) in one-dimensional normalized rectangular coordinates can be written

$$\frac{d^2 y}{dz^2} = k^2 \sinh y \quad (72)$$

In (72) k produces damping of the fields. As an example, a liquid with an ion density $c_0 = 6 \times 10^{24}$ ions m^{-3} , and $\varepsilon_r = 78$ yields $k \approx 2 \times 10^8 \text{ m}^{-1}$. This value of $1/k$ corresponds to a skin depth of 5 nm.

The boundary conditions for (72) are

$$y(z=0) \equiv y_0 = \frac{z_c q \psi_0}{k_B T} \quad (73)$$

where ψ_0 is the potential on the boundary, and

$$\lim_{z \rightarrow \infty} y(z) = 0 \quad (74)$$

$$\lim_{z \rightarrow \infty} \frac{dy}{dz}(z) = 0 \quad (75)$$

The integrals of the Poisson-Boltzmann equation are well known, but are reproduced here for later comparison [8]. The first integral is

$$\frac{dy}{dz} = -2k \sinh(y/2) \quad (76)$$

and the second is

$$y(z) = 4 \tanh^{-1} [\tanh(y_0/4) e^{-kz}] \quad (77)$$

or

$$y(z) = \ln \left[\frac{e^{\frac{y_0}{2}} + 1 + (e^{\frac{y_0}{2}} - 1) e^{-kz}}{e^{\frac{y_0}{2}} + 1 - (e^{\frac{y_0}{2}} - 1) e^{-kz}} \right] \quad (78)$$

ACKNOWLEDGMENT

We would like to thank Stan Abramowitz of the Advanced Technology Program at NIST for support, Claude Weil, and the helpful remarks and patience of a reviewer.

REFERENCES

- [1] C. Grosse and V.N. Shilov, "On the possibility of inductive properties in suspensions of ion exchange resin particles", *J. Coll. Interface Sci.*, Vol. 178, pp. 18-28, 1996.
- [2] L. A. Rosen, J. C. Baygents, and D. A. Saville, "The interpretation of dielectric response measurements on colloid dispersions using the dynamic Stern layer model", *J. Chem. Phys.*, Vol. 98, pp. 4183-4194, 1992.
- [3] G. R. Pack, G. A. Garrett, L. Wong, and G. Lamm, "The effect of a variable dielectric coefficient and finite ion size on Poisson-Boltzmann calculations of DNA-electrolyte systems", *Biophys. J.*, Vol. 65, pp. 1363-1370, 1993.
- [4] C. G. an Raquel Barchini, "The influence of diffusion on the dielectric properties of suspensions of conductive spherical particles in an electrolyte", *J. Phys. D. Appl. Phys.*, Vol. 25, pp. 508-515, 1992.
- [5] F. W. Wiegel and P. Strating, "Distribution of electrolytes with excluded Volume around a charged DNA molecule", *Mod. Phys. Lett. B*, Vol. 7, pp. 483-490, 1993.
- [6] N. Olcer, "On the theory of conductive heat transfer in finite regions", *Int. J. Heat Mass Transfer*, Vol. 7, pp. 307-314, 1964.
- [7] S. S. Dukhin and V. N. Shilov, *Dielectric Phenomena and the Double layer in Disperse Systems and Polyelectrolytes*, John Wiley and Sons, 1973.
- [8] C. M. A. Brett and A. M. O. Brett, *Electrochemistry*, Oxford Science Publications, 1993.
- [9] P. Strating and F. W. Wiegel, "Distribution of ions around a charged sphere", *Physica A*, Vol. 193, pp. 413-420, 1993.
- [10] M. D. Frank-Kamenetskii, V. V. Anshelevich, and A. V. Lukashin, "Polyelectrolyte model of DNA", *Biopolymers*, Vol. 30, pp. 317-330, 1987.
- [11] C. E. Galindo and J. B. Sokoloff, "Uncoiling transition for DNA in solution", *Phys. Rev. E*, Vol. 54, pp. 691-705, 1996.
- [12] K. Zakrzewska, A. Madami, and R. Lavery, "Poisson-Boltzmann calculations for nucleic acids and nucleic acids complexes", *J. Chem. Phys.*, Vol. 204, pp. 263-269, 1996.

¹ Opinions, interpretations, conclusions, and recommendations are those of the author and not necessarily endorsed by the United States Air Force.

Manuscript was received on 28 August 1998, in final form 17 February 1999.